Surface Enhanced Resonance Raman Scattering of Cetyl Orange LB Monolayers (Commemoration Issue Dedicated to Professor Natsu Uyeda, on the Occasion of His Retirment)

AUTHOR(S):

Takenaka, Tohru; Umemura, Junzo; Nakagawa, Tetsuo

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 66, No. 5, 1988

Surface Enhanced Resonance Raman Scattering of Cetyl Orange LB Monolayers

Tohru TAKENAKA*, Junzo UMEMURA*
and Tetsuo NAKAGAWA*

Received October 24, 1988

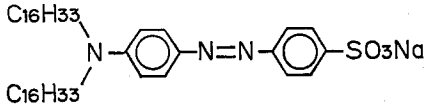
Surface enhanced resonance Raman scattering (SERRS) from a single LB monolayer of cetyl orange with evaporated Ag films was observed. The contribution of the surface enhanced Raman (SER) effect to the overall enhancement was determined. Results of studies on the enhancement factor, the excitation profiles, the Ag thickness dependence, and the distance dependence of the SERS indicate the importance of the electromagnetic interacton between the LB monolayer and surface plasma resonance of the Ag islands.

KEY WORDS: SERRS/ SERS/ LB monolayer/ Cetyl orange/ Ag evaporation/

I. INTRODUCTION

Recently, studies of surface enhanced Raman scattering (SERS) have been extended to Langmuir-Blodgett (LB) films deposited on rough metal surfaces.[1-3] Since LB films have well-defined molecular concentrations at precise distance from the metal surface, they have been used to explore the distance dependence of the SERS enhancement factor from the metal surfaces.

On the other hand, Raman scattering from dye molecules adsorbed on rough metal surfaces has been known to give an enormous intensity enhancement due to overlapped contributions from SER effect and resonance Raman (RR) effect, and then referred to as surface enhanced resonance Raman scattering (SERRS).[4-7]



Cetyl Orange

In the present study, we observed SERRS from a single LB monolayer of cetyl orange with evaporated Ag films and extracted the contribution of the SER effect to the overall enhancement by eliminating that of the RR effect. In addition, the enhancement factors, the excitation profiles, the Ag thickness dependence, and the distance dependence of the SERS were determined. From the results obtained, the importance of the electromagnetic mechanism to SERS of our system was demonstrated.

* 竹中 亨, 梅村純三, 中川徹夫 : Laboratory of Surface Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611.

II. EXPERIMENTAL

Cetyl orange was the same as that described previously.[8] Water used as a subphase was purified by a modified Mitamura Riken automatic lab still consisting of a reverse osmosis module, an ion-exchange column, and a double disitiller, and adjusted to pH 10 by sodium hydroxide (Wako Pure Chemicals, GR grade). The cetyl orange monolayer spread on the water surface from a chloroform solution (1.0×10^{-3} M) was compressed at 10°C to the surface pressure of 35 mN/m, at which the monolayer was in a solid-condensed phase,[8] and transferred onto solid substrates by the standard LB method.[9] The moving speed of the solid substrates was fixed at 10 mm/min. The observed transfer ratio was always very close to unity.

The Ag films with mass thicknesses thinner than 20 nm were vacuum-evaporated on the cetyl orange monolayer deposited on a Si plate in an Ulvac Model EBH-6 evaporator at 2×10^{-6} Torr. The evaporation rate was 1×10^{-2} nm/sec. The mass thickness of the Ag films was monitored by an Ulvac Model CRTM thickness gauge with an oscillating quartz crystal.

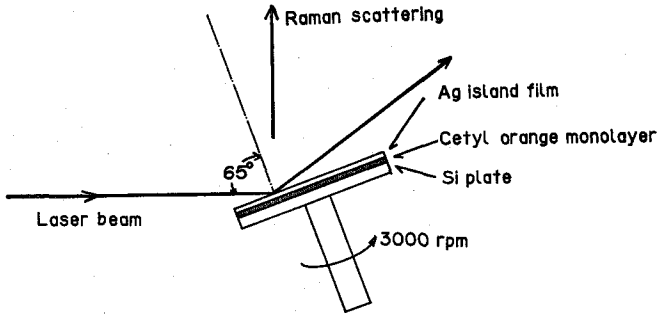


Fig. 1. Experimental geometry for SERR spectral measurements of the Ag-evaporated cetyl orange monolayer deposited on a Si plate.

Figure 1 shows the experimental geometry used for SERR spectral measurements of the above-mentioned cetyl orange monolayer with the evaporated Ag film. The excitation line from a Spectra Physics Model 164-03 Ar^+ laser or a Coherent Model Inova-90 Kr^+ laser was incident upon the film surface as shown in this figure. Raman scattering was observed in the direction perpendicular to the excitation line and recorded on a Spex Triplemate equipped with a Seki Model OMD-1000 V intensified photodiode array detector. The sample on the Si plate was rotated at 3,000 rpm to avoid photodecomposition. For Raman intensity measurements, the 520-cm^{-1} peak of Si was used as a reference standard after corrections for the wavelength-dependent sensitivity of the Raman instrument.

Absorption spectra were observed on a Hitachi Model 200-10 spectrophotometer.

III. RESULTS AND DISCUSSION

Figure 2(a) is the absorption spectrum of the Ag film with 2-nm mass thickness

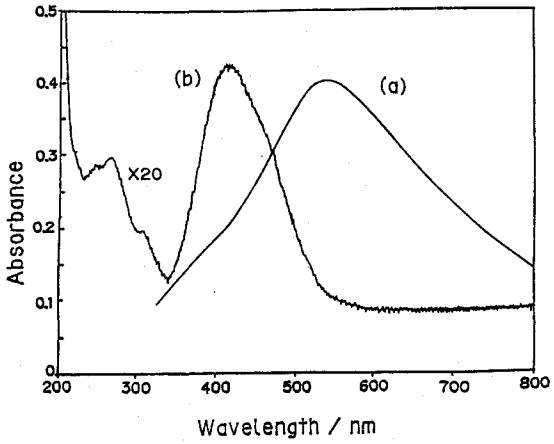


Fig. 2. Absorption spectra of (a) the Ag film (2-nm mass thickness) evaporated on the cetyl orange monolayer deposited on a quartz plate, and (b) the cetyl orange LB monolayer on a quartz plate.

evaporated on the cetyl orange monolayer deposited on a quartz plate. A maximum around 540 nm is due to the surface plasmon resonance of the Ag islands.[10] Figure 2(b) represents the absorption spectrum of the cetyl orange LB monolayer deposited on a quartz plate. A maximum at 413 nm has been assigned to the lowest π-π^* transition of the *trans* azobenzene moiety with the transition moment parallel to the long axis of the chromophore.

Figure 3(a) is the RR spectrum of the cast film of cetyl orange with 200-monolayer thickness prepared on a Si plate. Figure 3(b), on the other hand, shows the SERR spectrum of the Ag-evaporated cetyl orange monolayer deposited

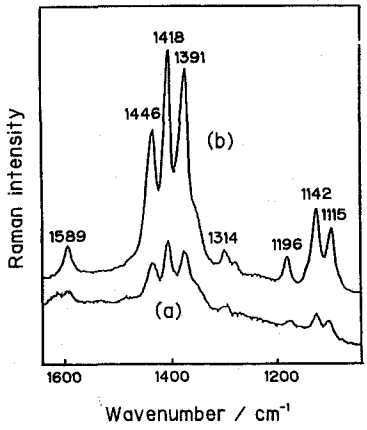


Fig. 3. (a) RR spectrum of the cast film of cetyl orange with 200-monolayer thickness prepared on a Si plate. (b) SERR spectrum of the Ag-evaporated (2 nm) cetyl orange LB monolayer deposited on a Si plate. 488.0 nm Excitation.

on a Si plate. The mass thickness of the Ag film was 2 nm. In spite of the fact that the thickness of cetyl orange in the LB monolayer is 1/200 of that in the cast film, the Raman intensities are much larger in the (b) spectrum than in the (a) spectrum. This result indicates that the evaporation of the Ag film to 2-nm mass thickness gives rise to a great intensity enhancement due to the SER effect. It is to be noted that peak positions and relative intensities of cetyl orange in the (b) spectrum remain almost identical with those in the (a) spectrum. This fact suggests that there is no particular chemical bonding of cetyl orange to evaporated Ag. This may simply rule out the possibility of the intensity enhancement by the

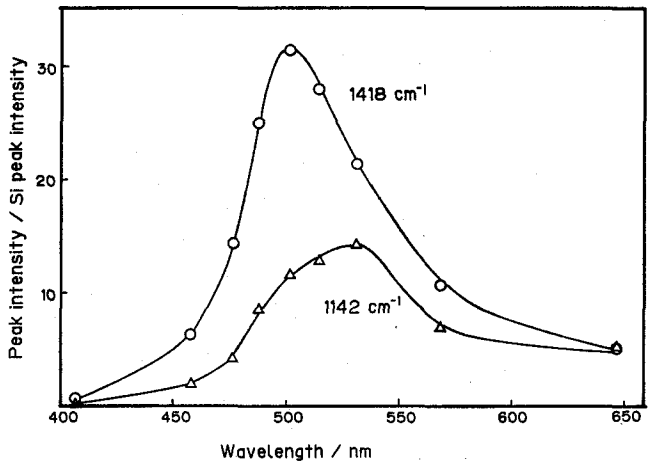


Fig. 4. Excitation profiles of the SERRS intensity of the 1,418- and 1,142-cm^{-1} peaks obtained from the Ag-evaporated (2 nm) cetyl orange LB monolayer.

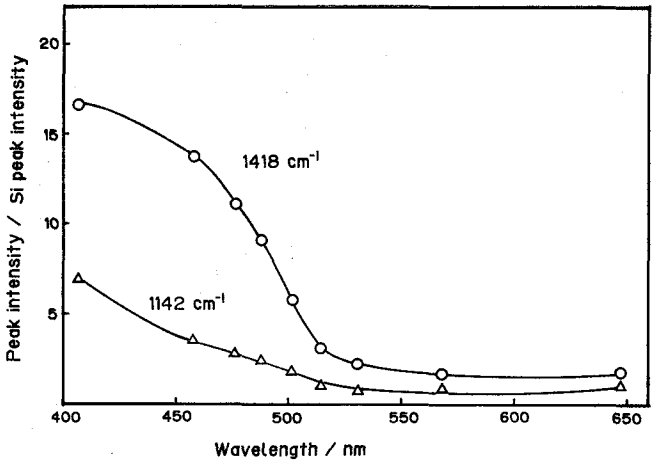


Fig. 5. Excitation profiles of the RRS intensity of the 1,418- and 1,142-cm^{-1} peaks obtained from the cast film of cetyl orange with 200-monolayer thickness.

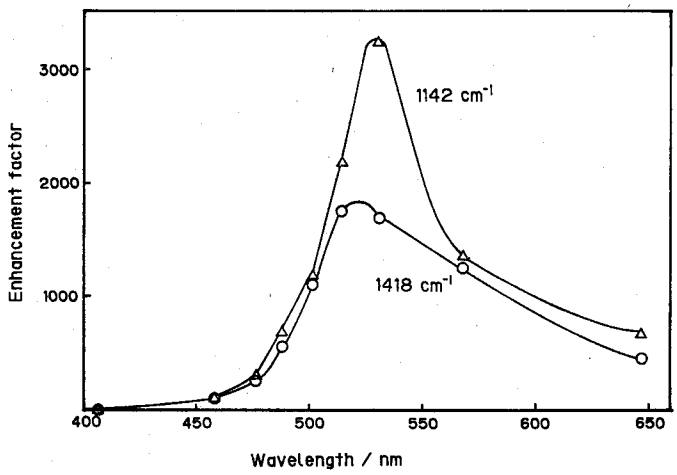


Fig. 6. Wavelength dependence of the SERS enhancement factors of the 1,418- and 1,142-cm^{-1} peaks obtained from the Ag-evaporated (2 nm) cetyl orange monolayer.

chemical mechanism.

Hereafter, the observations of the SERS will be made for the two major Raman peaks of cetyl orange at 1,418 and 1,142 cm^{-1} which have been assigned to the N=N stretching and Ph-N stretching vibrations, respectively.[8] Figure 4 is the excitation profiles of the SERRS obtained from the Ag-evaporated cetyl orange monolayer on a Si plate. For both peaks of cetyl orange, the curves maximize between 500 and 530 nm. Figure 5, on the other hand, illustrates the excitation profiles of the RRS from the cast film of cetyl orange with 200-monolayer thickness prepared on a Si plate. The curves for both vibrational modes rise in the shorter wavelength region toward the above-mentioned absorption maximum of cetyl orange at 413 nm (Fig. 2(b)).

Since the observed excitation profiles of the SERRS contain both contributions from the SER effect and RR effect, in order to illustrate the excitation profile of the SERS, we have to eliminate the contribution from the RR effect of cetyl orange by normalizing the Raman intensities of the Ag-evaporated cetyl orange monolayer with those of the cast film of cetyl orange with the 1-monolayer thickness without Ag film. The latter intensities were evaluated as 1/200 of those of the cast film of the 200-monolayer thickness, since the linear relationship was observed between the Raman intensity and the cast film thickness. The results are shown in Fig. 6. The enhancement factors of the SERS for both Raman modes exhibit the maxima around 530 nm, being in good agreement with the absorption maximum around 540 nm (Fig. 2(a)), which has been ascribed to the surface plasmon resonance of the Ag islands. The maximum values of the enhancement factors are roughly between 2,000 and 3,000 depending on the vibrational modes. These values are comparatively low as compared with the typical enhancement factor of the SERS (*ca.* 10^5), but are of the same order of magnitude as the theoretical ones calculated by Weitz et al.[11] under the assumption of the electromagnetic

interaction between adsorbed molecules and the surface plasma resonance of the Ag islands.

In order to demonstrate the importance of the roughness of the Ag film surface in the SERS, we examined the Ag thickness dependence of the Raman intensities. The Ag films of various thickness thinner than 20 nm were evaporated onto the cetyl orange monolayer deposited on a Si plate. Raman excitation was performed by the use of 530.9 nm line of the Kr^+ laser which is close to the maximum of the excitation profile of the SERS (Fig. 6). As shown in Fig. 7, maximum enhancements were obtained at a mass thickness of 7 nm, where the evaporated Ag film was known to consist of closely packed islands with the uniform diameter about 30 nm.[12] The electric field is maximumly enhanced on Ag islands around this diameter.

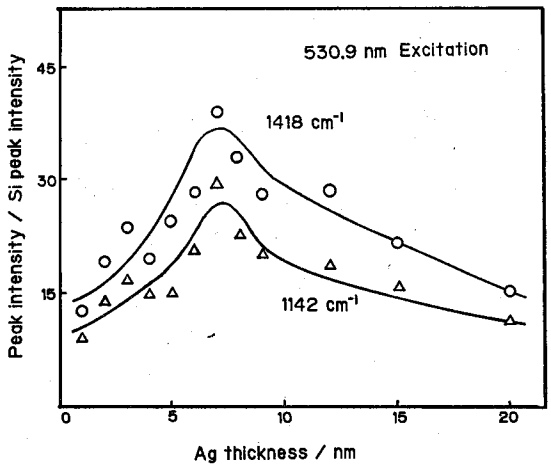


Fig. 7. Ag thickness dependence of the SERRS intensity of the 1,418- and 1,142-cm^{-1} peaks obtained from the Ag-evaporated (2 nm) cetyl orange LB monolayer. 530.9 nm Excitation.

Finally, we examined the distance dependence of the SERRS enhancement factor for the cetyl orange monolayers. In this part of experiment, we first evaporated the Ag island film to a mass thickness of 7 nm on a Si plate. Then, cadmium stearate LB films of less than 14 monolayers were deposited on the Ag-evaporated Si plate, and finally covered with two LB monolayers of cetyl orange.* The cadmium stearate films serve as spacer layers to control the separation distance between the Ag film and cetyl orange monolayers. The results are shown in Fig. 8. Similar to the distance dependence reported by Kovacs et al.[2] and Cotton et al.,[3] the enhancement factors exponentially decreased with increasing the number of spacer layers, that is, with increasing the distance between the Ag film and the cetyl orange monolayers. This fact apparently indicates the long range nature of

* In these tranfer processes, the horizontal lifting method[13] was used because the Ag film was peeled off when the solid substrate was immersed in water by the LB method.

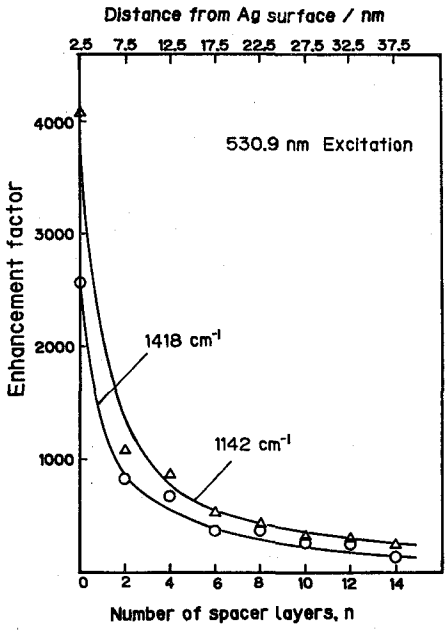


Fig. 8. Dependence of the SERRS enhancement factors of the 1,418- and 1,142-cm^{-1} peaks of cetyl orange on the number of spacer layers between the Ag film and the cetyl orange monolayers. 530.9 nm Excitation.

the SERS. Thus we can conclude that the SERS in our system is due to the electromagnetic mechanism and rule out a chemical mechanism which would require direct contact between the cetyl orange monolayers and the Ag films.

IV. SUMMARY

We observed the SERRS from the single LB monolayer of cetyl orange with evaporated Ag films, and determined the enhancement factors, the excitation profiles, the Ag-thickness dependence, and the distance dependence of the SERS. The results are as follows.

1) There were no distinct differences of the peak position and relative intensities between the SERR spectrum of the Ag-evaporated cetyl orange monolayer and the RR spectrum of the cast film without Ag film. This indicates the physical interaction between the cetyl orange monolayer and the Ag film, and rules out the possiblity of the Raman intensity enhancement by the chemical mechanism.

2) The maximum enhancement factors of the SERS were between 2,000 and 3,000, being of the same order of magnitude as the theoretical values based on an electromagnetic field enhancement mechanism.

3) The maxima of the excitation profiles of SERS were around 530 nm which is in good agreement with the absorption maximum around 540 nm due to the surface plasmon resonance of the Ag islands.

4) The maximum enhancement of the SERS was obtained at 7-nm mass thickness

of the evaporated Ag film which is known to consist of closely packed islands with diameter about 30 nm. The electric field is enhanced at its maximum on Ag islands around this diameter.

5) The enhancement factor of the SERS decreased exponentially with increasing the number of spacer layers between the Ag film and cetyl orange monolayers.

These results lead us to the conclusion that the electromagnetic mechanism is responsible for the SERS in this system. Further, the above results illustrate that LB monolayers can provide useful means to have important informations about the nature of SERS.

REFERENCES

(1) R. Aroca, C. Jennings, G.J. Kovacs, R.O. Loutfy and P.S. Vincett, *J. Phys. Chem.*, **89**, 4051 (1985).
(2) G.J. Kovacs, R.O. Loutfy, P.S. Vincett, C. Jennings and R. Aroca, *Langmuir*, **2**, 689 (1986).
(3) T.M. Cotton, R.A. Uphaus and D. Möbius, *J. Phys. Chem.*, **90**, 6071 (1986).
(4) R.P. Van Duyne, in "Chemical and Biochemical Applications of Lasers", Ed. by C.B. Moore, Vol. 4, Academic Press, New York (1979).
(5) T. Watanabe and B. Pettinger, *Chem. Phys. Letters*, **89**, 501 (1982).
(6) E. Burstein, G. Burns and F.H. Dacol, *Solid State Commun.*, **46**, 595 (1983).
(7) Y.C. Chou, N.T. Liang and W.S. Tse, *J. Raman Spectrosc.*, **17**, 481 (1986).
(8) T. Takenaka and H. Fukuzaki, *J. Raman Spectrosc.*, **8**, 151 (1979).
(9) K.B. Blodgett, *J. Am. Chem. Soc.*, **56**, 495 (1934); **57**, 1007 (1935).
(10) C.G. Blatchford, J.R. Campbell and J.R. Creighton, *Surface Soi.*, **120**, 435 (1982).
(11) D.A. Weitz, S. Garoff, J.I. Gersten and A. Nitzan, *J. Chem. Phys.*, **78**, 5324 (1983).
(12) T. Kamata, A. Kato, J. Umemura and T. Takenaka, *Langmuir*, **3**, 1150 (1987).
(13) T. Kamata, J. Umemura and T. Takenaka, *Chem. Letters*, 1231 (1988).